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TRANSPORT IN THERMALLY GROWN SILICA ON SILICON

J. Bruce Wagner, Jr.

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

January 1980

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TRANSPORT IN THERMALLY GROWN SILICA ON SILICON

INTRODUCTION

Computer modeling of the oxidation step in silicon integrated circuit (IC) device processing requires an improved understanding of the nature of oxidant transport and the oxidation mechanism, on a microscopic scale, so that an accurate mathematical description can be formulated. The oxidation of silicon has developed along three almost separate paths. The first is the very high temperature oxidation from about 1100°C to above the melting point, 1420°C, where the oxidation may involve volatile SiO gaseous species and transport through a boundary layer may be rate determining.¹⁻³ The second is the high temperature oxidation from about 900 to 1200°C in which a thick layer of silica separates the reactants and a decrease in rate with time is observed. The studies in this regime have generally been directed to protection of ceramics and metals.⁴⁺ Frequently the material studied has been impure silicon or silicon carbide or silicon nitride. The kinetics have generally been described as parabolic,

$$x^2 = k_T t$$

where x denotes film thickness, t the time, and k_T is the Tamman parabolic rate constant expressed in units of cm^2/sec . The most extensive studies have been carried out at lower temperatures, about 500 to 1000°C, on relatively pure, well-oriented single crystals for the electronics industry. In this regime, the mixed linear-parabolic kinetic model first described by U.R. Evans⁵⁺ and applied especially to silicon by Deal and Grove⁶⁺ is supposed to hold. The advantage of the single-crystal, lower-temperature studies is that the materials are well-characterized and controlled. The advantage of the higher temperature studies is that the role of minor impurities should be of less influence because of the thermal disorder in the grown silica layer. The very high temperature work will not be considered further here inasmuch as transport through a solid silica layer is the aim of this report.

KINETIC EQUATIONS

The equation for the mixed linear-parabolic model due to Deal and Grove⁶⁺ is in integrated form,

$$x^2 + Ax = B(t + \tau)$$

where

$$A = 2D_{\text{eff}}[1/k + 1/h]$$

$$B = 2D_{\text{eff}}C^*/N_1$$

$$\tau = (x_1^2 + Ax_1)/B$$

x = thickness of SiO_2 at any time, t

x_1 = thickness of oxide on Si initially present prior to onset of kinetic study, $x = x_1$ at $t = 0$

D_{eff} = effective diffusion coefficient for species migrating through SiO_2

+ See list of references on page 12.

k = rate constant

h = rate constant

C^* = concentration of oxygen at the O_2 - SiO_2 interface

N_1 = number of oxidant molecules incorporated into a unit volume of oxide layer.

In the limit of thick films ($x \rightarrow \infty$, $t \rightarrow \infty$) this equation should approach the simple parabolic rate expression

$$x^2 \cong Bt = k_T t$$

for $\Delta x \ll x^2$

and $\tau \ll t$.

The oxidation kinetics have been studied by many investigators.^{4,5,7-19†} Most of the data have been obtained at one or near one atmosphere oxygen pressure. When parabolic kinetics are observed, generally diffusion of the species across the reaction product layer is rate determining. Under such conditions and when there is virtual equilibrium at the metal-oxide interface and at the oxide-gas interface, the classical equation for oxidation of metals by C. Wagner^{20,21†} may apply. Using the Tamman rate expression

$$x^2 = k_T t,$$

it can be shown that,

$$\frac{k_T}{v} = k_r = \frac{1}{F^2} \int_{\mu_O'}^{\mu_O''} \frac{(\sigma_{ion}) \sigma_{elec}}{|Z_O| \sigma} d\mu_O$$

where

k_r = rational rate constant in $eq/cm^2 \text{ sec}$

v = equivalent volume (eq wt/density)

N_0 = Avogadro's number

F = Faraday constant

σ = total conductivity = $\sigma_{ion} + \sigma_{elec}$

μ_O' = chemical potential of nonmetal (in this case oxygen) at the metal-oxide interface (Si - SiO_2 interface)

μ_O'' = chemical potential of oxygen at the SiO_2 -gas interface

Z_O = valence of oxygen in SiO_2

† See list of references on page 12.

σ_{ion} = ionic conductivity = $\sigma_{\text{Si}} + \sigma_{\text{O}}$ in SiO_2

σ_{elec} = electronic conductivity in SiO_2 .

In order to test the applicability of the C. Wagner model, information is needed concerning the values of σ_{ion} and σ_{elec} as a function of oxygen potential, $\mu_{\text{O}} = \mu_{\text{O}}^{\circ} + RT \ln p_{\text{O}_2}^{1/2}$.

Three types of data are needed. These are

1. isothermal, isobaric oxidation kinetics to test whether the parabolic, mixed linear parabolic or other rate equation holds.
2. isothermal oxidation kinetics as a function of oxygen partial pressure. These data can be used to test an oxidation mechanism according to Fueki and Wagner.^{22†}
3. isothermal ionic and electronic conductivity of SiO_2 as a function of chemical potential of oxygen.

ELECTRICAL CONDUCTIVITY AND IDENTIFICATION OF MIGRATING SPECIES

Additionally, the diffusing species should be identified. Marker studies^{7,10,23-26†} have indicated that the migrating species through the silica layer is most likely oxygen and not silicon. The charge on the oxygen and whether it is a single atom or a molecule is a matter of controversy.

Deal and Grove^{6†} suggested that the migrating species was the peroxide ion, O_2^- . Others have suggested that the oxygen molecule is uncharged or that an interstitial oxygen ion, O_i'' , is the dominant species. These cases will be discussed further below. Jorgensen^{24,27-29†} carried out a series of classical papers using an applied electric field to accelerate and to retard (depending on the polarity) oxidation of silicon and of other metals. The fact that an applied electric field could accelerate or retard the oxidation rate was accepted by many authors as evidence that the oxygen species possessed a negative charge or charges. However, Raleigh³⁰ pointed out that this was not necessarily the case. An applied electric field could result in electrolysis of the oxide film and the existence of a charged species could not be unambiguously determined from such experiments alone. Mills and Kröger^{31†} carried out experiments on silica to obtain the total, ionic and electronic conductivity. They used the following configurations:

Cell I	<table><tr><td>Si</td><td>SiO₂</td><td>Si</td></tr></table>	Si	SiO ₂	Si
Si	SiO ₂	Si		
Cell II	<table><tr><td>Si</td><td>SiO₂</td><td>Ge_{1-x}Si_x</td></tr></table>	Si	SiO ₂	Ge _{1-x} Si _x
Si	SiO ₂	Ge _{1-x} Si _x		
Cell III	<table><tr><td>Si</td><td>SiO₂</td></tr></table> PO ₂	Si	SiO ₂	
Si	SiO ₂			

† See list of references on page 12.

Cell I is a symmetrical cell in which the chemical potential of silicon has its lowest value ($a_{Si} = 1$). Current-voltage characteristics were used to obtain the total conductivity, σ (ionic plus electronic; $\sigma = \sigma_{ion} + \sigma_{elec}$) using this cell. The results from this particular cell have been criticized on the basis that the dielectric breakdown of silicon was exceeded. An approximate check on this can be made as follows. The dielectric strength of SiO_2 is $\sim 5 \times 10^6$ volts/cm³²⁺ presumably at 25°C. The thickness of Mills and Kröger's films was 3000 Å and the applied voltage was 0.1 to 10 volts. Hence the field they applied was

$$\frac{\Delta V}{x} \text{ in } \frac{\text{volts}}{\text{cm}} = (0.1 \text{ to } 10) : 3000 \times 10^{-8} = 3 \times 10^5 \text{ to } 3 \times 10^4 \text{ volts/cm.}$$

The temperature range Mills and Kröger used was 150°C and above. This simple calculation indicates their measurements at the elevated temperatures approached the dielectric breakdown strength and hence further tests of this cell using different oxide thicknesses would be highly desirable.

Cell II is an asymmetrical cell for measuring the open circuit potential, E , (the emf at infinite impedance) across a layer of SiO_2 . This voltage is related to the oxygen pressure by

$$E = \frac{RT}{F} \int_{p_{O_2}'}^{p_{O_2}''} \left[\frac{t_{ion}}{n} \right] d \ln p_{O_2}$$

where F = Faraday's constant

p_{O_2}' , p_{O_2}'' = oxygen partial pressure at the $Si-SiO_2$ and at the $SiO_2-Ge_{1-x}Si_x$ phase boundaries, respectively

t_{ion} = transport number for ions

n = number of equivalents transported for a reaction involving 1 gm mole O_2 . If $O^=$ is the migrating species then $n=4$.

Thus by varying the p_{O_2}'' (changing the value of x in the alloy $Ge_{1-x}Si_x$) the isothermal ionic transport number as a function of oxygen pressure or Si/O ratio can be obtained.

Cell III is an analogous asymmetric cell to Cell II and the same principles apply.

Therefore if the total conductivity can be obtained from Cell I and the ionic transport number from Cell II or Cell III, then the ionic conductivity, σ_{ion} , may be obtained as

$$\sigma_{ion} = \sigma t_{ion}$$

and the information used to test the applicability of C. Wagner's equation plus an indication of the state of charge on the migrating oxygen (the value of n in the equation above).

† See list of references on page 12.

Three sets of data are available for this purpose: the data of Mills and Kröger^{31†} cited above, the analysis of Jorgensen's data by Raleigh^{30†} and a report by Tripp et al.^{4†} The problem is that if one extrapolates these data to a common temperature of 850°C, the data of Mills and Kröger and of Tripp et al differ by one order of magnitude and that of Jorgensen by four or five orders of magnitude. Furthermore, none of the measured conductivity data allow even an order of magnitude calculation of the rate of oxidation. In addition, the state of charge on the oxygen atom or molecule is not clear.^{31†}

ANALYSIS OF OXIDATION KINETICS

A reevaluation of the basic oxidation kinetics is needed. Deal and Grove,^{6†} Ligenza,^{10†} Hess and Deal,^{11†} Attala,^{7†} Lavery and Ryan,^{12†} Tripp et al,^{4†} Flint,^{8†} and Nakayama and Collins^{33†} all report parabolic or mixed linear parabolic kinetics to best represent the oxidation data.

The oxygen pressure dependence of the oxidation kinetics may also be used to test the mechanism and the charge on the diffusing species. Table 1 lists available information concerning the oxygen pressure dependence of the rate. For the most part the rate is proportional to $P_{O_2}^m$ where $0.75 \leq m \leq 1$. Recently, Zeto^{34†} completed a study of the dry high pressure oxidation of silicon (up to 500 atmospheres) and showed that

$$x^{1/0.7} = x^{1.4286} = k_Z t$$

for isothermal, isobaric oxidation. Furthermore

$$k_Z \propto P_{O_2}^{0.7}$$

The lattice defects in SiO_2 can be formally represented as point defects in an ionic compound. These are listed in Table 2. The nonstoichiometric defects corresponding to simple point defects are listed in Table 3.

Irene very graciously supplied Zeto a copy of his data,^{18†} film thickness versus time, for three temperatures, 780, 893 and 980°C, for oxidation of (100) silicon wafers in dry (< 1 ppm $H_2O(g)$) oxygen ($P_{O_2} = 1$ atm).

Irene and van der Meulen^{18†} reported that the following equation well represented the data beyond an initial thickness, x_0 ($50 \leq x_0 \leq 380$ Å) depending on the temperature:

$$(t-t_0) = A'(x-x_0) + B'(x^2-x_0^2)$$

where A' = reciprocal of the linear rate constant

B' = reciprocal of the parabolic rate constant

x_0, t_0 = film thickness and time prior to the onset of the mixed linear parabolic model

† See list of references on page 12.

TABLE I

Dependence of oxidation rate on oxygen partial pressure

Authors	Ref.	Pressure range (atm)	Temperature range (°C)	Comments
Zeto	(1978) ^{34†}	77.7 to 500	700 to 900	Rate $\propto p_{O_2}^{0.7}$
Hess and Deal	(1975) ^{11†}	0.02 to 1	1200	Parabolic rate $\propto p_{O_2}^1$
W.T. Tripp et al	(1975) ^{4†}	0.016 to 0.8	1200 to 1390	Parabolic rate $\propto p_{O_2}^{3/4}$
Lavery and Ryan	(1969) ^{12†}	0.13 to 1	850 and 1200	Parabolic rate $\propto p_{O_2}^1$
Revesz	(1965) ^{15†}	10^{-2} to 10^{-1} 10^{-1} to 1		Rate $\propto \log p_{O_2}$ Rate $\propto \exp \log p_{O_2}$
Ligenza and Spitzer	(1960) ^{10†}	~ 0.01 to 1	700 to 1100	Parabolic rate $\propto p_{O_2}^{4/5}$
Flint	(1962) ^{8†}	0.1 to 1	1000 to 1200	Parabolic rate $\propto p_{O_2}^1$
Law	(1957) ^{9†}	1.3×10^{-6} to 6.6×10^{-5}	1000 to 1300	Rate $\propto \ln p_{O_2}$ but thin (100 to 1000 Å) oxides where space charge controlled kinetics

† See list of references on page 12.

TABLE 2

Formal representation of possible lattice disorder in stoichiometric SiO_2 assuming the charge on the silicon defect is four and the charge on the oxygen defect is two. (Diatomic oxygen species are not considered here, see Table 3.)

Disorder Type	Lattice Defects	Electroneutrality condition	Mass Action Expression
Schottky	Cation vacancies and anion vacancies	$[V_{\text{Si}}^{4'}] = \frac{1}{2} [V_{\text{O}}^{''}]$	$K_S = [V_{\text{Si}}^{4'}] [V_{\text{O}}^{''}]^2$
Frenkel	Cation vacancies and interstitial cations	$[V_{\text{Si}}^{4'}] [Si_i^{4\circ}]$	$K_F = [V_{\text{Si}}^{4'}] [Si_i^{4\circ}]$
Anti-Schottky	Interstitial cations and interstitial anions	$[Si_i^{4\circ}] = \frac{1}{2} [O_i^{''}]$	$K_{A-S} = [Si_i^{4\circ}] [O_i^{''}]^2$
Anti-Frenkel	Interstitial anions and anion vacancies	$[O_i^{''}] = [V_{\text{O}}^{''}]$	$K_{A-F} = [O_i^{''}] [V_{\text{O}}^{''}]$
Anti-Structural	Cations on anion sites and anion on cation sites	$[Si_{\text{O}}^{6\circ}] = [O_{\text{Si}}^{6'}]$	$K_{\text{Anti-Str.}} = \frac{[Si_{\text{O}}^{6\circ}]}{[Si_{\text{O}}^{6\circ}] [O_{\text{Si}}^{6'}]}$

TABLE 3

Formal representation of nonstoichiometric
point defects in SiO_2

Interstitial species	Compensating electronic species	Electroneutrality condition	Oxygen pressure dependence
1. uncharged O_2	none	---	$p_{\text{O}_2}^1$
2. O_2'	h°	$[\text{O}_2'] = [h^\circ]$	$p_{\text{O}_2}^{1/2}$
3. O_2''	$2h^\circ$	$[\text{O}_2''] = \frac{1}{2}[h^\circ]$	$p_{\text{O}_2}^{1/3}$
4. O'	h°	$[\text{O}'] = [h^\circ]$	$p_{\text{O}_2}^{1/4}$
5. O''	$2h^\circ$	$[\text{O}''] = \frac{1}{2}[h^\circ]$	$p_{\text{O}_2}^{1/6}$

Note: There is the possibility that the concentrations of electronic defects, in these examples electron holes, are much less than the concentration of lattice defects. For example, in example 2, $[\text{O}_2'] = \text{constant} \gg [h^\circ]$. Hence the rate will depend on the diffusion of the electron holes and $[h^\circ] \propto p_{\text{O}_2}^{1/2}$. Likewise for example 3, $[h^\circ] \propto p_{\text{O}_2}^{1/2}$; for example 4, $[h^\circ] \propto p_{\text{O}_2}^{1/4}$ and for example 5, $[h^\circ] \propto p_{\text{O}_2}^{1/6}$.

On the other hand, the data were reanalyzed at Fort Monmouth and it was found that the simple equation

$$x^{1/0.7} = k_z t$$

in every instance represented the data to a greater degree of confidence on a least square analysis than did the mixed linear parabolic model of Deal and Grove^{6†} or of Irene and van der Meulen.^{18†} Moreover, use of the simple equation did not involve the discarding of any of the data points. In other words, all data points fitted the simple equation with greater confidence limits than did the mixed linear-parabolic which involved the discarding of the first data points in the thin film regime. Zeto^{34†} had found that all of his data, including thick film data (up to a micron and thicker) fitted the simple equation using all data points with much better confidence limits than any of the mixed linear-parabolic models.

Unfortunately, many of the literature references do not contain the raw data even in the form of small scale figures so a direct comparison with other data is not possible at this time. Another very important point is the role of water vapor on the oxidation kinetics. It is well-known that the presence of water vapor lowers the activation energy and increases the oxidation rate. But it was only recently determined that trace amounts of water vapor exert a large influence on the kinetics. Irene^{17†} has shown very conclusively that as little as 25 ppm water vapor in one atmosphere of oxygen can affect the oxidation kinetics.

As a result of Irene's studies as well as those of other researchers industry has adopted stringent requirements for the presence of water vapor. However, much of the data published prior to about 1975 must be examined critically because it was not known that traces of water influenced the kinetics to the extent demonstrated by Irene. Tripp *et al*^{4†} were aware of this problem and their high temperature (1200-1400°C) data follow the parabolic rate law, $x^2 = k_p t$, very well. One of these workers, H.C. Graham, provided copies of that group's raw data. Their data did not follow the equation,

$$x^{1/0.7} = k_z T.$$

Thus a most pressing need is for oxidation kinetics between about 700 and 1200°C in dry (< 1 ppm water vapor) oxygen.

The microstructure of the oxide should be examined as a function of time and temperature as well as oxygen pressure using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The conditions under which the two rate equations, $x^2 = k_p t$ and $x^{1/0.7} = k_z t$, hold must be settled. Concurrently, because the oxygen pressure dependence is not in accord with the simple defect models (see Tables 1 and 3), and because amorphous silica is a polymer or a glass (35-37) alternative models for transport should be sought. For example, polymeric materials may exhibit defects due to chain folds. Likewise the presence of micropores or channels must be tested.^{38†} Silica is very nearly stoichiometric. The excess oxygen, i.e., the oxygen in the silica layer at the silica-oxygen interface, has been reported^{6†} to be $5.2 \times 10^{16}/\text{CC}$ at 1000°C. This corresponds to about 0.0001 at. %

† See list of references on page 12.

excess oxygen. Consequently, small amounts of impurities may cause large changes in the rates of oxidation. Revesz and Evans¹⁹ demonstrated this effect dramatically by utilizing different reaction tubes, types of heating and sodium content. It is known that, e.g., traces of iron catalyze the crystallization of amorphous silica to cristobalite.⁴ The activation energies for oxidation when cristobalite forms increase but the rates are more rapid.⁴ This indicates the preexponential factor in the Arrhenius equation must also be changing dramatically. Again, a study of the microstructure and microchemical analysis of the silica layer is much needed. Also, a study of the effect of n and p substrates and an analysis of the incorporation of the dopants in the silica layer are needed. Here an ion milling unit and Auger analysis would be helpful. A summary of some of the activation energies reported for supposedly amorphous silica grown in supposedly dry oxygen is shown in Table 4. The energies fall into three categories. These are > 65 kcal (due to formation of cristobalite); > 40 kcal (in dry oxygen); and > 30 kcal or less (in moist oxygen).

SUMMARY

Based on the recent data of Zeto and analyses of literature data, there is a regime of oxidation kinetics which obeys the equation,

$$x^{1/0.7} = k_z t$$

with greater confidence limits than the simple parabolic or mixed-linear parabolic equations. Furthermore, the oxygen pressure dependence is

$$k_z \propto p_{O_2}^{0.7}$$

Neither the oxidation kinetics nor the oxygen pressure dependence are satisfactorily described by present models of the oxidation mechanism of silicon. Alternative models based on simple thermal lattice disorder or nonstoichiometric defects were formulated and also found to be unsatisfactory.

Analyses of available electrical conductivity data for thermally grown silica show discordant values for ion and electron conduction.

It is recommended that

1. Oxidation kinetics in dry (< 1 ppm H₂O) be obtained as a function of T and p_{O₂} with concurrent studies of the microstructure and chemical analyses of the silica.

2. The total, ionic and electronic conductivity be obtained on silica using cells of configurations listed in the text. Particular attention should be directed to low resistivity, ohmic contacts and to maintaining the I-V variables below dielectric breakdown strength of SiO₂.

† See list of references on page 12.

TABLE 4
Activation energies for oxidation of silicon to amorphous silica

Investigator	Ref.	Ea kcal	Ea ev	Temp. Range °C	Press. Range atm	Thickness Range	Orient.
Zeto	(1978) ^{34†}	~ 44	1.9	700 - 900	77.7 - 500	up to several microns	(100) & (111)
Irene & van der Meulen	(1976) ^{18†}	52.9* 29.9**	2.3* 1.5**	780 - 980	1	up to 2000 Å	(100)
Tripp et al	(1975) ^{4†}	65	2.8	1250 - 1400	0.8	up to several microns	crystalite islands
Tripp et al	(1975) ^{4†}	28-30	1.2-1.3	1200 - 1400	1.3×10^{-3} to 0.8		(100)
Tripp et al	(1975) ^{4†}	28-30	1.2-1.3	1200 - 1400	1.3×10^{-3} to 0.8		(111)
Irene	(1974) ^{17†}	43.7	1.9	800 - 996	1	~ 1500 Å	(100)
Irene	(1974) ^{17†}	39.1	1.7	800 - 996	1	~ 1500 Å	(111)
Revesz & Evans	(1969) ^{19†}	27.6	1.2	900 - 1300	;	100 - 3300 Å	
Nakayama & Collins	(1966) ³³⁺	25.3* 75.9*	1.1* 3.3**	850 - 1217	0.13 - 0.66	up to 4000 Å	(111)
Deal & Grove	(1965) ^{6†}	28.5	1.24	800 - 1200	1	up to one micron	not specified
Ligenza & Spitzer	(1960) ^{10†}	40	1.74	700 - 1100	~ 0.01 to 1	unknown	not specified
Law	(1957) ⁹⁺	31	1.35	900 - 1150	0.03 - 0.5	100 - 1000 Å	
Law	(1957) ^{9†}	23	1.0	950 - 1100	1	100 - 1000 Å	

* Parabolic

** Linear

† See list of references on page 12.

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